Preparation and Properties of Pure Alkyl Glucosides, Maltosides and Maltotriosides

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ABSTRACT

Alkyl β-D-glycopyranosides composed of glucose, maltose or maltotriose attached to alkyl groups having from 4 to 18 carbon atoms were synthesized and tested for their physical and functional properties. Values are given for melting points, optical rotations, detergencies, critical micelle concentrations, surface tensions, interfacial surface tensions, Draves wetting tests and Ross Miles foam tests. Results show that maximum cleaning was obtained with maltosides attached to straight chain alkyl groups having from 12 to 15 carbon atoms.

INTRODUCTION

In 1970 Hughes and Lew (1) reported that alkyl polyglucosides offer a wide range of physical and functional properties which make them suitable for use as biodegradable surfactants, detergents and emulsifiers. More recently n-octyl β-D-glucopyranoside and other similar compounds have been used as detergents to solubilize membrane proteins and to study the hydrophobic requirements of several enzymes (2-12).

Synthesis of these compounds was first accomplished by Noller and Rockwell (13) using a rather complicated procedure developed by Koenigs and Knorr (14) in which sugars were first acetylated and then converted to the brominated peracetates. The alkyl group was added by reacting the desired alcohol with the brominated peracetate in the presence of silver oxide, and deacetylation was accomplished by treatment with sodium methylate. Later modifications of this procedure (2,12,15,16,17) led to simplified preparations of alkyl glycosides with increased yields.

In 1965 Boettner (18) reported an alternative synthesis of alkyl glucosides involving a double alcohol interchange in the presence of an acid catalyst. Glucose was first converted to methyl glucoside, then to butyl glucoside, and finally to the desired alkyl glucoside. Later Mansfield (19) successfully prepared several alkyl glucosides and alkyl oligosaccharide mixtures directly from glucose and higher molecular weight alcohols by carefully controlling the removal of water during the reaction.

This paper describes the synthesis of a homologous series of alkyl glycosides containing glucose, maltose, isomaltose, cellobiose, or maltotriose as the sugar components with alcohol chains which range from 4 to 18 carbon atoms in length, and the measurement of the physical and functional properties of these molecules.

MATERIALS AND METHODS

Melting points were determined with a standard Fisher-Johns Melting Point Apparatus and are uncorrected. Optical rotation measurements were made at 25 C using a Rudolph polarimeter with methanol as a solvent and sodium light. Surface tension was measured at 25 C with a Cenco-du Nouy tensiometer according to the method described by Osipow (20), and critical micelle concentrations (CMC) were determined from a plot of the surface tension versus the log of the surfactant concentration (20). Interfacial surface tension was measured at 25 C using light mineral oil according to the procedure described in the Cenco-du Nouy Tensiometer Operation Instructions. Draves skein wetting tests were carried out using 0.1% aqueous solutions at ambient temperature according to AATCC Method No. 17-1980 (21). Ross Miles foam tests were done according to ASTM Method No. D1173-53 (22) using 0.1% solutions.

Cleaning tests. Cleaning tests were carried out using Dacron/cotton (65/35) and cotton swatches soiled with a dust-sebum soil (Scientific Services, Oakland, New Jersey 07436). Three swatches of Dacron/cotton and cotton were used in each cleaning test which was done in a Model 7243-S Terg-O-Tometer. Synthetic hard water (1000 ml) containing 0.118 g of $MgSO_4 \cdot 7 H_2O$ and 0.106 g $CaCl_2 \cdot 2 H_2O$ was heated to 40.6-43.3 C, and 0.45 g of surfactant was added. The resulting solution was allowed to agitate at 125 rpm for 30 sec before swatches were added. After washing for 15 min, swatches were removed, squeezed to remove excess surfactant solution, rinsed in 4 liters of tap water (38 C) for 5 min, and then dried in a clothes dryer for 15 min. L, a and b reflectance values of the swatches before and after washing were determined using a Hunter Labscan Spectrocolorimeter. The increase in reflectance of the swatches (L-washed minus L-soiled) represents the cleaning value of the surfactant. Cleaning values for a standard nonionic surfactant (Neodol 25-7, Shell Oil Company, Houston, Texas 77001) were 20.0 ± 0.6 for Dacron/cotton and 19.5 ± 0.5 for cotton.

Sugar peracetates. α-D-Cellobiose octaacetate was purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin 53210. All other peracetates were synthesized from glucose, maltose monohydrate (Difco Laboratories, Detroit, Michigan 48232), or maltotriose (SIGMA Chemical Company, St. Louis, Missouri 63178) according to the procedure of Rosevear et al. (17) with one modification. Higher temperatures (110 C for maltose and 120 C for maltotriose) were needed for the complete acetylation of the di- and trisaccharides. Yields were all 95% or higher.

Alkyl glycosides. n-Octyl β-D-glucopyranoside and n-nonyl β-D-glucopyranoside were purchased from Calbiochem-Behring Corp., La Jolla, California 92037, and were used without further purification. All other alkyl glycosides were synthesized and purified using the method reported by Rosevear et al. (17) with several modifications. Typically 20.0 g of sugar peracetate were dissolved in 50 ml of glacial acetic acid followed by the addition of 50 ml of HBr (30% in acetic acid—Eastman Kodak Company, Rochester, New York 14650). The light yellow solution produced was stirred at room temperature for 45 min. Dichloromethane (200 ml) was added and the resulting solution was immediately poured over 300 ml of crushed ice. The dichloromethane layer containing the brominated sugar peracetate was washed once with 200 ml of deionized water, 3 times with 200 ml portions of cold saturated aqueous sodium bicarbonate solution, and 3 times with 200 ml portions of deionized water. This layer was finally dried over anhydrous magnesium sulfate (50 g) for 30 min and then filtered through a Celite pad.

The dichloromethane layer was transferred to a flask covered with aluminum foil, and fresh dichloromethane was added to adjust the total volume to approximately 280 ml. Fatty alcohol, 6.0 g of freshly prepared silver carbonate, 0.4 g iodine, and 20 g of 4 angstrom molecular sieves (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin 53233) were added. For the synthesis of alkyl glucosides, a

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mole ratio of 1:1 (fatty alcohol:sugar peracetate) was used. This ratio was increased to 10:1 for the synthesis of the maltosides and maltotriosides because of improved yields at higher mole ratios (D. Koeltzow, manuscript in preparation). High levels of free alcohol interfere with the purification of alkyl glucosides.

After stirring overnight at room temperature, the mixture was filtered through a Celite pad and concentrated to a syrup on a rotary evaporator. Ortho esters were destroyed by treatment with 350 ml of 0.01 N H_2SO_4 in an acetone: water (90:10) mixture for 30 min at room temperature. For derivatives made from octadecanol, 150 ml of hexane were added to the acetone:water solution to aid in solubilizing the mixture. The resulting solution was neutralized with pyridine and concentrated to a syrup on a rotary evaporator.

Deacetylation was carried out by treatment of the sample with 400 ml of methanol:triethylamine:water (2:1:1) at room temperature for 48 hr. Compounds containing tridecyl or higher molecular weight alkyl groups required 72 hr for complete deacetylation. Solubility problems with the octadecyl compounds required that 650 ml of a mixture containing methanol:triethylamine:water: hexane (7:3:1:2) be used for the deacetylation of n-octadecyl β-D-maltopyranoside heptaacetate and 800 ml of the methanol:triethylamine:water mixture listed above be used for the deacetylation of n-octadecyl β-D-maltotriopyranoside decaacetate.

The branched tridecanol used in this study was a mixture of primary alcohols which contained methyl branches and was provided by the Enjay Chemical Company, New York, New York 10020. All of the other alcohols were commercially available as 97 to 99% pure compounds and were used without further purification.

Purification of alkyl glycosides. The Dowex 1 (OH$^-$ form) chromatographic method developed by Austin et al. (23) and modified by Rosevear et al. (17) was used to purify all of the synthesized alkyl glycosides. This process separated the α and β anomers, and the purity of the compounds obtained was verified by thin layer chromatography (TLC), reverse-phase high performance liquid chromatography (HPLC), and proton nuclear magnetic resonance (NMR). Low solubilities of the pentadecyl and octadecyl compounds in methanol required that these substances be purified on jacketed columns which were maintained at 40 C.

Butyl α-D-maltopyranoside was obtained from the Dowex 1 purification of butyl β-D-maltopyranoside. Fractions containing only the α anomer were pooled, concentrated to dryness, resuspended in water and freeze dried.

RESULTS AND DISCUSSION

Physical Parameters

Optical rotation and melting point data for all of the alkyl glycosides synthesized are given in Table I. As expected (12,13,25), none of the compounds produced have single sharp melting points; however, there are 2 distinct melting temperature regions. As these compounds are heated, they first change from a white opaque solid to a rather clear soft form which holds its shape. The temperature at which this occurs is referred to as the "softening point" in Table I and probably is the point at which the van der Waals forces between the alkyl chains are disrupted. Those compounds with high levels of nonpolar alkyl groups per sugar unit such as the alkyl glucosides have sharp softening point ranges of 0.5 to 1.0 degrees. The tridecyl compounds containing branched tridecyl groups have softening points

TABLE I

Physical Properties of Alkyl Glycosides

	Melting points (C)				
Compound	Softening point	Flow point	Literature value	$[\alpha]_D^{25}$	Literature value
n-Butyl α-D-maltopyranoside	63-65	Decomp-167	–	+178.4	–
n-Butyl β-D-maltopyranoside	67-70	Decomp-169	–	+33.8	–
n-Butyl β-D-maltotriopyranoside	126--	Decomp-185	–	+97.6	–
n-Decyl β-D-glucopyranoside	67-68	104-114	75-130(13)	–36.2	–27.8(13,16)
n-Decyl β-D-maltopyranoside	86--	156-159	81-126(12)	+44.0	–
n-Decyl β-D-maltotriopyranoside	137--	185-185.5	–	+96.1	–
n-Undecyl β-D-glucopyranoside	71-72	113-119	76.5-77.5(16)	–26.4	–26.4(16)
n-Dodecyl β-D-glucopyranoside	76-76.5	125-127	77-137(13)	–23.5	–24.7(13)
n-Dodecyl β-D-maltopyranoside	87-112	187-192	104-105(16)	+45.9	+47.7(16)
n-Dodecyl β-D-isomaltopyranoside	129--	157-157.5	–	+36.1	–
n-Dodecyl β-D-cellobiopyranoside	152-152.5	198-208	228.5(24)	–16.9	–41.8(24)
n-Dodecyl β-D-maltotriopyranoside	185--	217-217.5	–	+80.8	–
n-Tridecyl β-D-glucopyranoside	77-78	107-127	–	–2.3	–
n-Tridecyl β-D-maltopyranoside	83-108	181-190	–	+46.3	–
n-Tridecyl β-D-maltotriopyranoside	183--	200-200.5	–	+78.3	–
b-Tridecyl β-D-glucopyranoside	<25	70-85	–	–	–
b-Tridecyl β-D-maltopyranoside	64-89	173-197	–	+43.4	–
b-Tridecyl β-D-maltotriopyranoside	130--	172-173	–	+80.1	–
n-Pentadecyl β-D-glucopyranoside	76-76.5	102-122	–	–22.2	–
n-Pentadecyl β-D-maltopyranoside	82-86	171-198	–	+43.3	–
n-Pentadecyl β-D-maltotriopyranoside	133-143	179-180	–	+77.2	–
n-Octadecyl β-D-maltopyranoside	76-91	188-Decomp 210	–	+56.1	–
n-Octadecyl β-D-maltotriopyranoside	119-130	Decomp-230	–	+72.1	–

which are from 20 to over 50 degrees lower than those of the compounds made with n-tridecanol. The softening point ranges of the alkyl maltosides or maltotriosides are much broader and, while it is easy to determine the temperature at which softening begins, it is often impossible to tell when softening is complete.

On continued heating of the material, a second melting temperature, the "flow point," is reached when the softened compound becomes a liquid and begins to flow. This point is representative of the disruption of the hydrogen bonding between the carbohydrate portions of the molecules. The flow point range is sharp for the alkyl maltotriosides which are relatively high in carbohydrate content. However, it is broad for most of the alkyl glucosides requiring several degrees between the temperature at which the compound first begins to flow and the temperature at which all of the compound is a liquid.

These data are consistent with the liquid crystal properties of n-nonyl and n-decyl β-D-glucopyranoside and other alkyl glycosides reported by Jeffrey and Bhattacharjee in 1983 (25). Published X-ray and differential-scanning-colorimeter thermogram data suggest that, when heated, these compounds pass from the crystalline phase through an intermediate phase, a liquid crystal phase, and finally reach a liquid phase. The different melting point data reported here support this multiphase transition for all of the alkyl glycosides studied except the n-butyl derivatives.

The optical rotation data given are the expected values of the various alpha and beta anomers and indicate that the length of the alkyl group has little effect on the amount of rotation. As the number of alpha linkages in a molecule are increased, the rotation becomes more positive.

Butyl α-D-maltopyranoside was the only alpha anomer which was purified for melting point and optical rotation measurements. However, small quantities of alpha anomers were produced for all of the compounds made by the synthetic procedure used here. It should be noted that these anomers have properties which are quite different from those of the beta anomers. They are extremely hygroscopic and, because of this, they are difficult to work with.

Cleaning Activity

The results of cleaning tests using Dacron/cotton and cotton swatches are shown in Figure 1. These data clearly show that optimal cleaning for both types of swatches requires a maltoside (DP-2) attached to an alkyl group containing from 12 to 15 carbon atoms. This is in close agreement with the results of McGuire and Matson (26) and McFarland and Kinkel (27), who reported that the highest detergency values for alcohol ethoxylate surfactants were obtained with alcohol chain lengths of from 12 to 15 carbon atoms. The DP-2 compounds containing 12 to 15 carbon atoms in the alkyl chain range from 62 to 67% glucose, which also agrees with the 70% ethylene oxide content needed for maximum cleaning with ethoxylate surfactants reported by McGuire and Matson (26).

It is interesting to note that dodecyl β-D-cellobiopyranoside shows the same cleaning ability as the maltopyranoside or the isomaltopyranoside for both cotton and Dacron/cotton fabrics in spite of its markedly lower water solubility. Also surprising is the effect of the branching in the tridecyl compounds. Branched tridecyl β-D-glucopyranoside (DP-1) and maltotriopyranoside (DP-3) are noticeably poorer surfactants than the unbranched tridecyl compounds, particularly in the case of the Dacron/cotton swatches. Finally it should be pointed out that these compounds clean Dacron/cotton swatches slightly better (1 to 2 detergency units) than the cotton swatches.

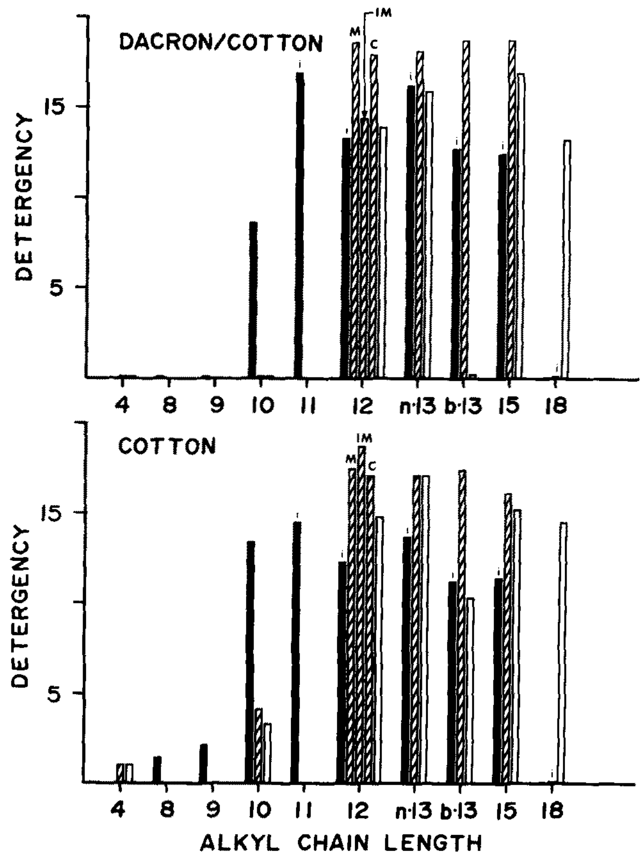

FIG. 1. Detergency values. Alkyl glucosides—■; alkyl disaccharides—▨. (The disaccharide attached to all alkyl groups was maltose except for the C-12 alkyl group where M = maltose, IM = isomaltose, and C = cellobiose). Alkyl maltotriosides—☐. An "i" indicates that a compound was not completely soluble at the concentration used for a particular test. Alkyl b-13 is a branched tridecyl mixture.

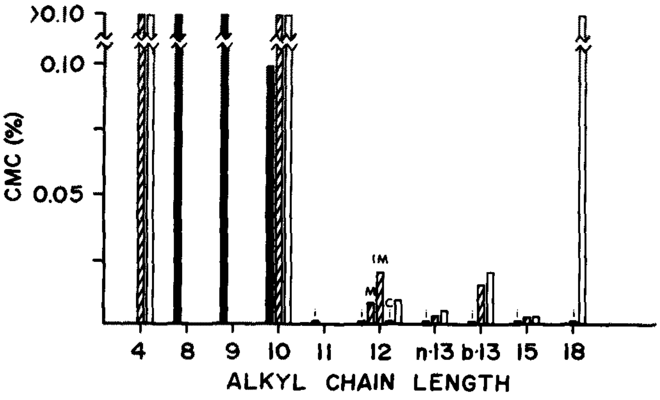

FIG. 2. Critical micelle concentrations. See Figure 1 for an explanation of symbols.

Critical micelle concentrations (CMC) for the alkyl glycosides studied are shown in Figure 2 and correlate with the cleaning ability of these compounds. A lower CMC value means a higher concentration of micelles on a per weight basis for a given surfactant and, therefore, generally indicates better cleaning capability. However, it should be noted that while branched tridecyl β-D-maltotriopyranoside shows a low CMC value, it is a very poor cleaner and therefore, low CMC values are not always indicative of high cleaning ability.

The surface tension and interfacial surface tension values

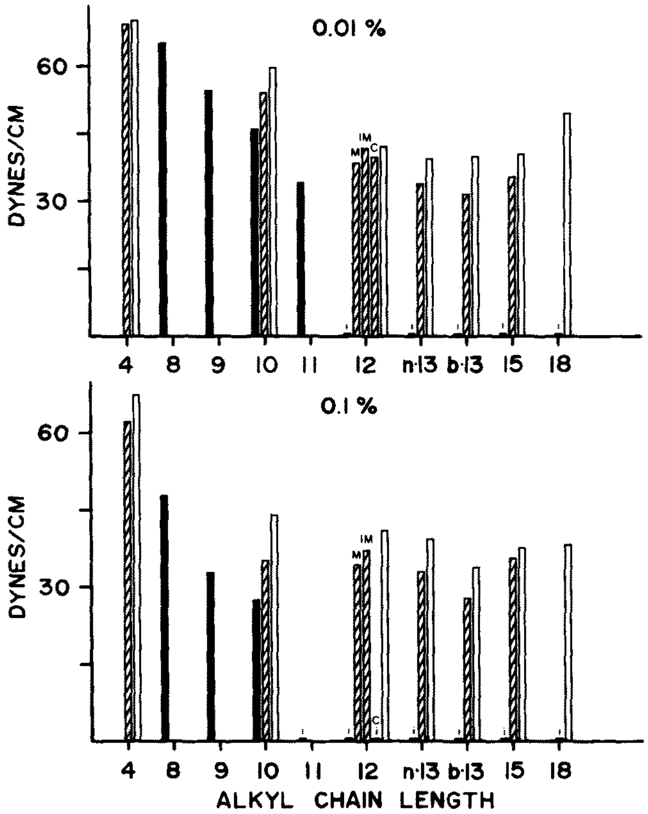

FIG. 3. Surface tension values. See Figure 1 for an explanation of symbols.

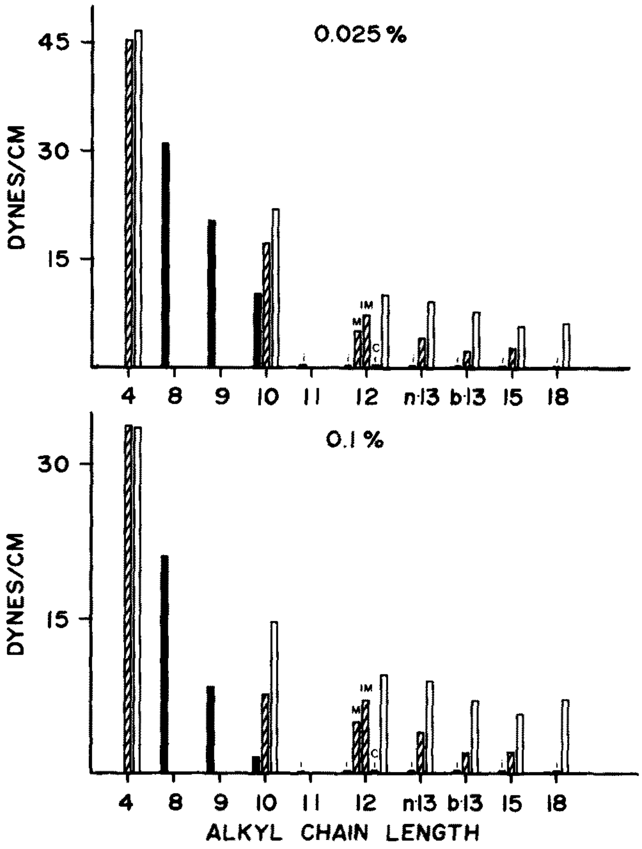

FIG. 4. Interfacial surface tension values. See Figure 1 for an explanation of symbols.

TABLE II

Ross Miles Foam Test

Compound	Foam height (mm)[a]	
	0 Minutes	5 Minutes
n-Butyl β-D-maltopyranoside	5	0
n-Butyl β-D-maltotriopyranoside	0	0
n-Nonyl β-D-glucopyranoside	45	15
n-Decyl β-D-glucopyranoside	155	150
n-Decyl β-D-maltopyranoside	140	140
n-Decyl β-D-maltotriopyranoside	142	138
n-Undecyl β-D-glucopyranoside	I	I
n-Dodecyl β-D-glucopyranoside	I	I
n-Dodecyl β-D-maltopyranoside	148	145
n-Dodecyl β-D-maltotriopyranoside	140	140
n-Tridecyl β-D-glucopyranoside	I	I
n-Tridecyl β-D-maltopyranoside	130	120
n-Tridecyl β-D-maltotriopyranoside	130	130
b-Tridecyl β-D-glucopyranoside	I	I
b-Tridecyl β-D-maltopyranoside	165	164
b-Tridecyl β-D-maltotriopyranoside	170	165
n-Pentadecyl β-D-glucopyranoside	I	I
n-Pentadecyl β-D-maltopyranoside	78	78
n-Pentadecyl β-D-maltotriopyranoside	80	80
n-Octadecyl β-D-maltopyranoside	I	I
n-Octadecyl β-D-maltotriopyranoside	23	23

[a] I indicates that the compound is not soluble in water at the 0.1% level.

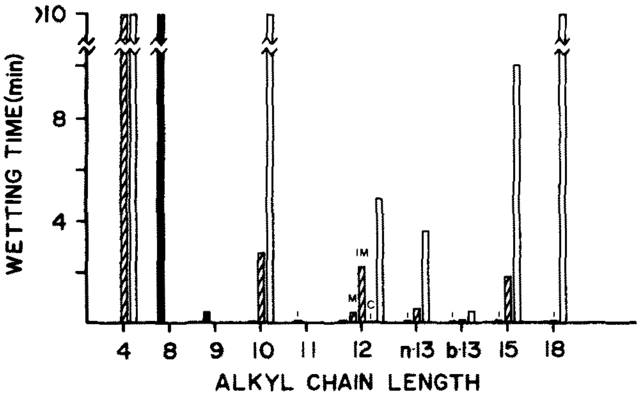

FIG. 5. Draves wetting tests. See Figure 1 for an explanation of symbols.

shown in Figures 3 and 4 respectively are typical of many nonionic surfactants. Surface tension measurements of 30 to 40 dynes/cm, which are thought to be required for good cleaning, are obtained by low concentrations (0.01%) of the DP-2 and DP-3 compounds containing 12 to 15 carbon atoms in the alkyl chain. Low interfacial surface tensions were achieved by this same group of compounds which indicates their effectiveness at penetrating oils. Low values mean that less mechanical energy is required to release the soil. One notable exception to this trend is decyl β-D-glucopyranoside which shows a very low interfacial surface tension value (1.6 dynes/cm at 0.1%) and a low detergency.

The results of the Draves wetting tests shown in Figure 5 also match the cleaning efficiencies found. In general those compounds with shorter wetting times have higher detergency values. However, the nonyl and decyl β-D-glucopyranosides along with the decyl β-D-maltopyranoside are noticeable exceptions.

Two important trends in wetting times are indicated by these data. For any alkyl chain length, the glucoside has the fastest wetting time followed by the maltoside with the maltotrioside having the slowest wetting time. Secondly, wetting times tend to decrease as the alkyl chain length increases with glucosides reaching a minimum at C-10, maltosides at C-12 and maltotriosides at C-13. Branched tridecyl β-D-maltopyranoside and maltotriopyranoside show faster wetting times than the unbranched tridecyl compounds.

The Ross Miles foam test results given in Table II indicate that those compounds containing alkyl chain lengths from 10 to 13 carbon atoms produce stable foams. It is also interesting to note that the number of glucosyl groups (up to DP-3) attached to an alcohol does not affect the foam production or its stability.

The above data show that alkyl glycosides which contain 12 to 15 carbon alkyl chains attached to maltose have the necessary CMC, surface tension, interfacial surface tension and wetting properties to make them effective surfactants. Members of this class of compounds exhibit the properties needed for a wide range of applications.

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